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14. ABSTRACT Nanocomposites of graphene or graphene oxide and either metal nanoparticles or macroporous copper oxides (macroCuO) were synthesized and their electrochemical properties and possible applications investigated. MacroCuO with graphene was successfully used as supercapacitor electrode material. Electrochemical measurements of this system revealed the maximum specific capacitance, energy density and power density of 417 F g^{-1}, 58 Wh kg^{-1} and 17.85 kWkg^{-1}, respectively at a current density of 0.9 Ag^{-1}. Graphene/silver nanoparticle/polypyrole modified glassy carbon electrode (Gr-AgNPs-PPy-GCE) was synthesized and its use as a supercapacitor electrode is under investigation. Graphene (Gr)-gold nanoparticles (AuNP)-Nafion and silver nanoparticle (AgNP)/graphene oxide (GO) composites have been successfully synthesized and characterized. These materials were investigated as supercapacitor electrodes with different electrolytes. AuNP-Nafion was found to be useful for sensing the pharmaceutical molecule Sumatriptan, and AgNP/GO shows high sensitivity in detection of Arsenic.

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Abstract:

Nanocomposites consisting of graphene/graphene oxide and metal (Ag, Au) nanoparticles/macroporous copper oxides (macroCuO) were synthesized using different green routes and their electrochemical properties were investigated. These nanocomposites have demonstrated wider applications viz., supercapacitors and electrochemical sensors. The nanocomposite of macroCuO with graphene has been successfully used as supercapacitor electrode material for energy storage. Electrochemical measurements of this system revealed the maximum specific capacitance, energy density and power density of 417 F g^1, 58 Wh kg^1 and 17.85 kWkg^{-1}, respectively at a current density of 0.9 Ag^{-1}.

Synthesis and characterization of graphene/silver nanoparticle/ polypyrole modified glassy carbon electrode (Gr-AgNPs-PPy-GCE) has also been achieved and it's utilization as an electrode material for supercapacitor applications is in progress.Graphene (Gr)-gold nanoparticles (AuNP)-Nafion and silver nanoparticles (AgNP)/graphene oxide (GO) composites have been successfully synthesized and characterized. These materials were investigated as electrodes for supercapacitors using different supporting electrolytes. These materials also offer excellent electrochemical sensing properties for the detection of certain pharmaceutical molecules and trace elements. Specifically, graphene (Gr)-gold nanoparticles (AuNP)-Nafion composite is found to be useful for sensing a pharmaceutical molecule, Sumatriptan, and AgNP/graphene oxide (GO) composite shows high sensitivity electrochemical detection of Arsenic.

Introduction:

Nanomaterials of different shapes, sizes, and compositions, have found broad applications in analytical methods and in energy storage devices. Among the various energy storage devices, supercapacitors (SCs), also known as electrochemical capacitors, have attracted considerable attention over the past decade due to their high power density, fast charging/discharging rate, and long cycle life comparing to secondary batteries and conventional dielectric capacitors Among the different materials, metallic nanoparticles, metal oxides, polymers and the composites of these nanoparticles with carbonaceous materials like graphene, graphene oxide or carbon nanotubes are of immense interest due to their unique electronic, optical, electrical and electrochemical properties with potential applications in a wide range of technologies including supercapacitors, besides chemical and

biochemical sensors. Metal nanoparticle-modified electrodes show dramatically enhanced electrochemical sensitivity due to their large specific surface area and high surface free energy. Besides, sensing they provide a very high surface area for electrical double layer formation. Some metallic oxides and metallic compounds, such as cobalt oxide, gold and platinum nanoparticles have already been reported to be suitable for electrode modifications. However, such electrodes are costly, display low efficiency which hinders their commercial applications.

On the other hand, transition metal oxides or hydroxides with variable valence, such as NiO, Co_3O_4, MnO_2, $Ni(OH)_2$ and CuO can provide higher energy density for supercapacitor. Such materials not only store energy like electrostatic carbon materials but also exhibit electrochemical faradaic reactions between electrode materials and ions within appropriate potential windows. Porous materials like, porous copper oxide (CuO) is noteworthy to be explored as a promising candidate due to its low cost, abundant resources, non-toxicity, chemically stable, and easy preparation in diverse shapes of nano-sized dimension which offers both a cost advantage and potentially a high performance benefiting from both mechanisms of electric double layer capacitance and pseudo-capacitance. The work on the performance of Graphene/ macroporos CuO composite as electrode material for supercapacitors is in progress.

Besides, the use of such materials as electrode for supercapacitors, they are also expected to be used in electrochemical sensors. In the present work, we have successfully synthesized the Graphene (Gr)-gold nanoparticles (AuNP)-Nafion composite which has been used for the subnanomolar determination of Sumatriptan (SUM). A silver nanoparticles (AgNPs)/graphene oxide (GO) composite has been synthesized using beta cyclodextrin as a stabilizing agent and ascorbic acid as a reducing agent and has been applied for the determination of As(III) in real water samples.

The use of the same electrode material for sensing as well as an electrode for supercapacitors is documented in literature. Therefore, our goal is to use such synthesized materials as electrodes for supercapacitors. It is expected that the results of the present study would result in the fabrication of supercapacitors with high power and energy density.

Experiment:

Preparation of graphene-gold nanoparticle-Nafion electrode

GO was synthesized directly from graphite by Hummers method. The synthesized graphite oxide powder was exfoliated in doubly distilled water by ultrasonication for 2h to form homogeneous GO dispersions with a concentration of 1.0 gL^{-1}. Graphene/AuNP

composite was prepared according to a literature procedure. For the preparation of graphene–gold nanocomposites, a mixture solution containing 10.0 mgL^{-1} GO and 0.24 mM HAuCl4 was prepared. The electro- chemical co-reduction was performed in the mixture solution under magnetic stirring using cyclic voltammetry. Here, the CV scan was performed between -1.5 and 0.6 Vat a rate of 25 mVs^{-1}. The thickness of the nanocomposite film was controlled by five potential cycles. It was observed that after electro-reduction, the surface of the GCE changed from black to bright red (color) of AuNPs), which indicated that AuNPs were deposited on to the electrode surface. After electrochemical co-reduction, the working electrode was washed with doubly distilled water and dried under I. R. lamp. Finally, Nafion modification was carried out by drop casting (7.0 mL, 0.1%) on to the surface of the GCE and the solvent was allowed to evaporate at room temperature.

Green synthesis of the AgNP/GO nanocomposite and preparation of the AgNP/GO/GCE

GO was synthesized from natural graphite powder by a modified Hummers'method. Firstly, GO powder (15.0 mg) was dispersed in water (15.0 mL) by sonication for 1h to form a stable GO colloid. Then 0.2 g β-cyclodextrin was added to 8.3 ml of 5% $AgNO_3$ and stirred. This solution was added to GO colloid while stirring. Then 10 ml of 2.6% ascorbic acid was added and a precipitate is formed. The precipitate was washed with water repeatedly to remove any impurities. Finally, the obtained product was dried over night in an oven at 60 ^{0}C, and then the AgNPs/GO nanocomposite was obtained.

The mixed suspension of 10.0 μL of above nanocomposite in DMF was cast onto the GCE surface by a micropipette, and then the suspension was thoroughly dried out under an infrared lamp. After that, the electrode was rinsed by distilled water for several times and further dried in air before use, and the final obtained electrode was denoted as AgNPs/GO/GCE.

Preparation of Graphene-Silver nanoparticle-Polypyrrole modified glassy carbon electrode (Gr/AgNP/PPy/GCE)

40 mg of graphene and 10 mg of silver nanoparticles were sonicated in 50 ml of distilled water for 30 mins. In this process the silver nanoparticles are deposited on the graphene sheets to form graphene-silver nanoparticles composite. To this 0.45 gm of pyrrole monomer is added and polymerization is carried out adding 50 ml of 6 mM $FeCl_3$. The mixture was kept at 4-9° for 24 hrs. The composite was filtered and washed firstly with distilled water then by alcohol to remove any impurity and was dried at 60° for 12 hrs.

The composite material of graphene-silver nanoparticles-polypyrrole was dispersed in ethanol (4 mg/ml ratio) and 10 µl suspension was deposited on to the glassy carbon electrode. The electrode was dried under an IR lamp. Before testing electrode was rinsed several times with distilled water and dried in air before use. So, the final electrode is denoted as Gr-AgNPs-PPy-GCE.

Synthesis of macroporous copper-oxide monoliths and GN/macroCuO nanocomposite

Porous copper-oxide monoliths were prepared by dissolving 2.0 g $Cu(NO_3)_2.3H_20$(50 wt%, Sigma-Aldrich) in 2.0 g of ultrapure water (50 wt%) and 2.0 g of Pluronic P-123 (14.81 wt%, $M_w = 5800$, Aldrich) in 11.5 g of ultrapure water (85.19 wt%) followed by addition of 2 g of TMB at 25 °C. The gel was heated for 1 h at 55 °C on a magnetic stirrer to form the paste which gradually became light blue in colour. The resulting gel was aged for 2-3 days at room temperature and then calcined at 650 °C for 2 h at a heating rate of 1 C/min followed by cooling at a rate of 1 C/min to room temperature in an ELLITE furnace

GNs and macroCuO composites in the ratio 1:1 by weight were dispersed in 100 ml of distilled water by ultrasonication for 1 h to obtain a homogeneous GNs/macroCuO suspension. Finally, the solid was filtered, and washed several times with distilled water and alcohol, dried at 100 ^{0}C for 12 h in a vacuum oven..10 mg of the composite was dispersed in 5 mL dimethylformamide which was sonicated in an ultrasound bath for 30 min to form a stable suspension. The suspension of 10.0 µL was cast onto the GCE surface by a micropipette, and then the suspension was thoroughly dried out under an infrared lamp. Subsequently, the electrode was rinsed by distilled water for several times and further dried in air before use; the final obtained electrode was denoted as GNs/macroCuO/GCE.

Characterization

Scanning electron microscopy (SEM) images were obtained from S-4800 field emission SEM system (FEI Quanta 200) operating at 20.0 kV equipped to perform elemental chemical analysis by energy dispersive X-ray spectroscopy (EDX).Transmission electron microscopy (TEM) micrographs were performed using a field emission transmission electron microscope (TEM)(JEOL JEM-2100F TEM/STEM, Oxford Instruments, USA) operated at 200 kV. XRD studies were carried out using Maxima 7000S XRD (Shimadzu, Japan).

All voltammetric and chrono experiments were performed on a CHI electrochemical workstation (CH Instruments Model CHI1100B series). Electrochemical impedance and chronopotentiometry measurements were performed using, Electrochemical Work Station,

model Autolab PGSTAT 30 using GPES software, version 4.9.005 and Frequency Response Analyser, software version 2.0, respectively.

Results and Discussion:

Graphene-gold nanoparticle-Nafion modified glassy carbon electrode (Gr/AuNP/NAF/GCE):

Characterization of the electrode material has been carried out by XRD, UV-Vis spectroscopy, scanning electron microscopy and EDX. The formation of graphnene and AuNP using electrochemical reduction of graphene oxide to graphene and $HAuCl_4$ to AuNPs was verified by scraping off the Gr/AuNP composite from the GCE surface and monitoring it by measuring the UV–Visible spectra of the solutions after diluting the sample with deionized water. Graphene oxide shows strong absorption peak at ca. 230 nm which corresponds to the π-π^* transition of the aromatic C-C bond. After electrochemical reduction, the peaks at ca. 275 nm correspond to a complete reduction of graphene oxide to graphene. Color of gold is attributed to surface plasmon resonance (SPR).The SPR band of gold appears at 539 nm, the first peak appears at ca. 270 nm while the second appears at ca. 540 nm. Thus it further confirms that graphene and AuNP were prepared by the electro-reduction process.

Further confirmation of the electro-reduction process was carried out by carrying out the XRD analysis for Gr/AuNP. Gr shows peaks at $2\theta=24.54°$ and $43.54°$, corresponding to its (0 0 2) and (1 1 1) reflections. On the other hand, AuNPs give five peaks at $38.1°$, $43.80°$, $64.50°$, $77.50°$and $81.66°$ which correspond to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes. XRD pattern further shows that gold nanoparticles are crystalline in nature and are face-centered cubic (fcc) in structure. The SEM image of final composite shows that the nafion film is uniformly coated on to the graphene and AuNPs surface and energy-dispersive X-ray spectrum for the final composite shows the following elements: C from graphene and nafion; Au from AuNPs and F, O, S from Nafion.

The characterization of the electrode surface has been carried out by means of cyclic voltammetry, electrochemical impedance spectroscopy, chronocoulometry. Gr/AuNP/NAF/ modified GCE was used for the determination of sumatriptan (SUM). By employing at pH 7.0 phosphate buffer, a twenty fold enhancement in the AdSDPV signal was observed as compared to bare GCE for sumatriptan. Under the optimized conditions, I_p (μA) was proportional to the SUM concentration in the range of 1.0×10^{-6} - 4.12×10^{-5}M ($R^2 = 0.9991$) and 2.14×10^{-9} - 1.0×10^{-6} M ($R^2 = 0.9954$) with a detection limit ($3\times$SD/s) of 7.03×10^{-10} M.

The practical analytical utilities of the modified electrode were demonstrated by the determination of SUM in pharmaceutical formulations, human urine and blood serum samples. This proposed method was validated by HPLC and the results are in agreement at the 95% confidence level.

Silver nanoparticles graphine oxide (AgNP/GO) nanocomposite glassy carbon electrode:

For the verification of successful synthesis of the AgNPs/GO nanocomposite, various characterization methods were employed, including SEM, TEM, EDX and XRD. The nanocomposite was successfully synthesized and loaded on graphene oxide sheets.

Electrochemical characterization of AgNP/GO/GCE:

Electrochemical characterization of AgNP/GO/GCE was carried out by electrochemical impedance spectroscopy (EIS) and chronocoulometry (CC). The EIS results show that the charge transfer resistance (R_{ct} = 226 Ω) of AgNPs/GO/GCE is lower than that of GO/GCE (R_{ct}= 259 Ω) and bare GCE (R_{ct} = 276 Ω). This can be attributed to the excellent electronic property and high surface area of GO and cyclodextrin stabilized silver nanoparticles, forming a fast electron conduction pathway between the electrode and the electrochemical probe. The electrochemical effective surface areas obtained by chronocoulometry (CC) are 0.295 cm^2 and 0.141cm^2 for AgNP/GO/GCE and GO/GCE which are approximately 3.0 and 2.0 times of that of bare GCE (0.079 cm^2), respectively.

Electrochemical behaviors of As (III) at nanostructured electrode

Cyclic voltammetry was used to investigate the electrocatalytic activity of the AgNPs/GO/GCE for the electrochemical behaviour of As (III). When the AgNP/GO nanocomposite was immobilized on GCE surface, the reduction peak enhanced significantly and the corresponding oxidation peak potential shifted negatively to 0.143 V vs. Ag/AgCl accompanying the oxidation peak current increased by about three times as compared to GO/GCE. Hence, the synergistic effect of the AgNPs and GO catalyses the electrochemical reaction of arsenic. This can be attributed to the good catalytic ability, large surface area of AgNP/GO/GCE which facilitates the accumulation of the arsenic at the surface of electrode and accelerate the electron transfer. CV studies also showed that the reduction of As (III) to As (0) and the oxidation of As (0) to As (III) are a surface-confined and diffusion-controlled processes, respectively.

Detection performance of the AgNP/GO/GC electrode and LOD under the optimum conditions

The detection performance of the modified electrode was carried out using more sensitive square wave anodic stripping voltammetry (SWASV). The detection limit, linear calibration range and sensitivity for arsenic determination at this modified electrode are comparable and even better than those obtained by using other modified electrodes based on metal or metal oxide nanoparticles.

Simultaneous detection of As (III) and Cu (II)

Determination of As (III) in natural water samples is a challenging task because of co-deposition of other metals, particularly Cu (II) which is the main interferent during stripping analysis and reduces the sensitivity of target ions. It is observed that there is no interference of Cu (II) in the concentration range upto 3.75×10^{-7}M, thus present method can be used for simultaneous determination of As (III) and Cu (II).

The calibration plot was obtained from the SW-ASV analysis for As (III) and Cu (II) and the equation of calibration graph for each metal is;

As (III): $Y = 0.203X + 9.886$ (n = 5, r^2= 0.933)

Cu (II): $Y = 0.167X - 1.108$ (n= 5, r^2= 0.985).

Effect of other interferences

We tried to study the performance of the nanostructured AgNPs/GO/GC electrode in presence of different materials. Thus, the developed electrode showed good performance for As (III) detection in the presence of interfering substances at the mentioned levels.

Accuracy and precision

The accuracy of the developed method was carried out by spiking with accurately weighed amounts (preanalyzed amounts) of arsenic. The mean percent recovery of 99.63 and 100.11 in intraday and interday assay and the values of mean relative error indicate the good accuracy of the method.

The precision of the developed method for arsenic was determined in five replicate analyses. The mean variation coefficient is 1.03% and 1.73% in intraday and interday assay, respectively. The results confirmed both the good precision of the proposed procedure and stability of the electrode.

Reproducibility and stability of the sensor

The reproducibility of the proposed approach was evaluated by intra- and inter-assay coefficients of variation. After a 90-day storage period, the sensor retained 94.1% of its initial current response. These results indicate that the sensor held satisfactory performances in reproducibility and stability, and would thus be applicable for the analysis of arsenic in real samples.

Determination of arsenic in real samples

The AgNPs/GO-modified GCE was used to detect arsenic in different water samples obtained from ground water of Andheri (East), and Panchganga River, Mumbai, India. The ground water samples (50 ml) were diluted to 0.1M H_2SO_4 for detection of arsenic by standard addition method. The measurements were performed five times. 4.844×10^{-8} M of As (III) was detected in samples of Panchganga River while As(III) was below the detection limit in the samples received from Andheri (East) ground water. Thus, a known quantity of 10.65×10^{-8} M of As (III) was added in Andheri (East) water sample; the average value found was 10.418×10^{-8} M. Thus a recovery of 97.88% was obtained. This observation validates the suitability of As (III) detection in water samples using the developed sensor.

High performance supercapacitor based on graphene-silver nanoparticles-polypyrrole nanocomposite coated on glassy carbon electrode:

Characterization of Gr-AgNP-PPy-GCE and electrochemical study

The characterization of the electrode is carried out using XRD, Energy dispersive spectroscopy FT-IR and SEM analysis. Electrochemical characterization is carried out using cyclic voltammetry, galvanostatic charge-discharge technique and electrochemical impedance spectroscopy.

XRD spectra of graphene shows two peaks at 2θ=24.54º and 43.54º, corresponding to its (002) and (111) reflections. Silver nanoparticles show four peaks at 38.03°, 46.18°, 63.43° and 77.18° correspond to (111), (200), (220) and (311) planes. Polypyrrole shows two peaks at 11.8° and 24.8° respectively. The SEM image of final composite shows that the silver nanoparticles are uniformly dispersed on graphene sheets as cluster along with polypyrrole. Energy-dispersive X-ray spectrum for the final composite shows the following elements: C from graphene and polypyrrole; Ag from AgNPs. The electrochemical study of the composite electrode is in process.

Electrochemical studies

A new hybrid material of double layer capacitive material graphene (GNS), pseudo capacitive polypyrrole (PPY) and highly conducting silver nanoparticles (AgNPs) has been studies. Graphene/Silver nanoparticles/ polypyrrole (GNS/AgNPs/PPY) composite has been synthesized by in *situ* oxidative polymerization of pyrrole in the presence of GNS and AgNPs. The different mass concentrations of AgNPs were utilized to improve the capacitive performance of supercapacitor. Characterization of the electrode material has been carried out

by X-ray diffraction, Raman spectroscopy, Thermal methods, Scanning electron microscopy (SEM) and Transmission electron microscopy. SEM images showed that PPY nanoparticles uniformly coated on graphene sheets along with AgNPs. Electrochemical characterization of the electrode surface has been carried out by means of cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. Remarkably, GNS/AgNPs/PPY exhibits specific capacitance of 450 F g^{-1} at current density of 0.9 mA g^{-1}, which is far better than GNS/PPY (288 F g^{-1}), AgNPs/PPY (216 F g^{-1}) and PPY (153 F g^{-1}). Furthermore, GNS/AgNPs/PPY shows high charge-discharge reversibility and retaining over 92.0% of its initial value after 1000 cycles. The cyclic stability of the composite is improved due to the synergistic effect of GNS, AgNPs and PPY.

Characterization of macroporous copper-oxide monoliths and GN/macroCuO nanocomposite and its electrochemical performance

A facile and cost-effective synthesis approach was used to prepare macro-structured porous copper oxide monoliths via modified Sol-Gel route. 1, 3, 5-trimethylbenzene (TMB) was used as an organic structural directing agent to enhance the pore size, pore volume, pore density and surface area of the resulting CuO hybrid with Pluronic P-123 as soft template. GNs/ macroCuO nanocomposite was prepared by ultrasonication of the GNs and macroCuO. Macroporous copper oxide (macroCuO) was characterized using powder X-ray diffraction (PXRD), Scanning electron microscopy (SEM), Brunauer-Emmet-Teller (BET) adsorption study, Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopic (FT-IR) and energy dispersive x-ray (EDX) studies. The synthesized GN/macroCuO composite was characterized by SEM and EDX studies. This material is expected to be a promising material for supercapacitor applications.

Summary and Conclusion

Graphene (Gr)-gold nanoparticle (AuNP)-Nafion and silver nanoparticles /graphene oxide (AgNPs-GO) composites have been successfully synthesized and characterized using different methods. The work involving these materials as electrodes for supercapacitors using different supporting electrolytes is in progress. In the meantime, due to their high specific surface area, electro-catalytic and adsorptive properties, these materials were investigated for their performance in electrochemical sensors. It is found that Gr/AuNP/NAF/GCE can be

used for the determination of subnanomolar levels of SUM using adsorptive stripping voltammetry. The method has been employed for the determination of SUM in pharmaceutical formulations, urine and blood serum samples. Because of the attractive properties of AgNPsGO composite including ease of synthesis, low toxicity, surface functionalities and excellent stability, its applicability for detecting trace levels of As (III) using anodic stripping voltammetry was investigated. The developed sensor showed a low detection limit and good working range, At the same time, its analytical characteristics outperformed most of the reported electrochemical sensors. Our AgNP/GO electrochemical sensor can detect As (III) in the presence of Cu and is very stable in the presence of relatively large amounts of surfactant and organic compounds which also make it hold great promise in the electroanalysis and electro-catalysis. The developed sensor has been successfully applied for the determination of As (III) in ground and river water samples which gave a good recovery showing its suitability for the determination of As (III) in natural water samples and other As (III) containing samples.

In addition,, macroporous copper oxide and its composite with graphene have also been synthesized. The incorporation of macroCuO into graphene layers is expected to improve electrolyte–electrode accessibility and electrode conductivity by reducing the agglomeration of GNs. GN/macroCuO composite has been prepared by ultrasonication of GNs and macroCuO. Using this composite as an electrode, a supercapacitor has been fabricated. The electrochemical properties of the fabricated supercapacitor are under investigation.

Also, the electrochemical performance of Gr-AgNPs-PPy-GCE composite as electrode material for supercapacitor is in progress.

GNS/AgNPs/PPY nanocomposites have been synthesized by in situ polymerization method. The insertion of GNS in the composite provides a large surface area for dispersing PPY and Ag reduces the electrical resistance of the polymer and increase electrical conductivity, and electrochemical storage capacity. Controlling the ratio of AgNPs to GNS is very important to obtain good electrochemical performance. SEM analysis reveals that PPY nanoparticles are uniformly coated on graphene sheets along with silver nanoparticles. XRD analysis shows that PPY is amorphous in nature and have average particles size of 13 nm. TGA analysis confirmed composite material has better thermal stability than PPY alone. The maximum specific capacitance obtained is 442 F g^{-1} at a current density of 0.9 mA g^{-1} in 1M

KCl electrolyte. The composite electrode showed very good stability even after 1000 charge-discharge cycles. After 1000 charge-discharge cycling test, electrode maintains 92.0% of its initial specific capacitance value. The enhanced specific capacitance of the material is due to the synergistic effect of three components viz; GNS, AgNPs and PPY. These results suggest that GNS/AgNPs/PPY composite electrode is quite suitable and a promising electrode material for high performance supercapacitor.

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1. Bankim J. Sanghavi, Pramod K. Kalambate, Shashi P. Karna, Ashwini K. Srivastava, Voltammetric determination of sumatriptan based on a graphene/gold nanoparticles/Nafion composite modified glassy carbon electrode, **Talanta**, 120 (2014) 1–9.

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3. Pramod K. Kalambate, Riyaz A. Dar, Shashi P. Karna and Ashwini K. Srivastava, High performance supercapacitor based on graphene-silver nanoparticles-polypyrrole nanocomposite coated on glassy carbon electrode, **J. Power Sources**, *276*, 262 - 270 (2015)

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5. Pramod K. Kalambate, Bankim J. Sanghavi, Shashi P. Karna and Ashwini K. Srivastava, Simultaneous voltammetric determination of paracetamol and domperidone based on a graphene/platinum nanoparticles/Nafion composite modified glassy carbon electrode, **Sens. and Act. B**, *213*, 285 – 294 (2015)

6. Bankim J. Sanghavi, Nayan. S. Gadhari, Pramod K. Kalambate, Shashi P. Karna and Ashwini K. Srivastava, Potentiometric stripping analysis of arsenic using a graphene paste electrode modified with thiacrown ether and gold nanoparticles **Microchimica Acta** (In Press) 2015

Other related publications from our group:

1. B. J. Sanghavi and A. K. Srivastava, Adsorptive stripping voltammetric determination of imipramine, trimipramine and desipramine employing titanium dioxide nanoparticles and amberlite XAD-2 modified glassy carbon paste electrode, **Analyst,** *138,* 1395-1404 (2013)

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3. A. K. Srivastava and R. Gaichore, Voltammetric determination of nifedipine using a β-cyclodextrin modified multi-walled carbon nanotube paste electrode, **Sens. and Act. B,** *188,* 1328-1337 (2013)

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